Dielectric fluctuations in force microscopy: Noncontact friction and frequency jitter

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(Received 4 March 2008; accepted 1 May 2008; published online 13 June 2008)

Electric force microscopy, in which a charged probe oscillates tens to hundreds of nanometers above a sample surface, provides direct mechanical detection of relaxation in molecular materials. Noncontact friction, the damping of the probe's motions, reflects the dielectric function at the resonant frequency of the probe, while fluctuations in the probe frequency are induced by slower molecular motions. We present a unified theoretical picture of both measurements, which relates the noncontact friction and the power spectrum of the frequency jitter to dielectric properties of the sample and to experimental geometry. Each observable is related to an equilibrium correlation function associated with electric field fluctuations, which is determined by two alternative, complementary strategies for a dielectric continuum model of the sample. The first method is based on the calculation of a response function associated with the polarization of the dielectric by a time-varying external charge distribution. The second approach employs a stochastic form of Maxwell's equations, which incorporate a fluctuating electric polarization, to compute directly the equilibrium correlation function in the absence of an external charge distribution. This approach includes effects associated with the propagation of radiation. In the experimentally relevant limit that the tip-sample distance is small compared to pertinent wavelengths of radiation, the two methods yield identical results. Measurements of the power spectrum of frequency fluctuations of an ultrasensitive cantilever together with measurements of the noncontact friction over a poly(methylmethacrylate) film are used to estimate the minimum experimentally detectable frequency jitter. The predicted jitter for this polymer is shown to exceed this threshold, demonstrating the feasibility of the measurement. © 2008 American Institute of Physics. [DOI: 10.1063/1.2932254]

I. INTRODUCTION

A wide range of dynamical phenomena in condensed matter may be understood with a picture in which the effects of a complex environment are represented by a fluctuating electric field. Such processes include electron transfer,^{1,2} enzyme kinetics,³ optical^{4–6} and vibrational^{7,8} spectroscopy, and ionic motion in solution.⁹ Electric field fluctuations at the interface between a solid surface and vacuum may be sensed with electric force microscopy,^{10–15} in which a charged probe oscillates close to the interface. The perturbation of the probe's dynamics by the presence of the surface provides direct mechanical detection of the fluctuating electric field produced by molecular motions in the sample. Two distinct experimental observables access electric field fluctuations of differing time scales. Measurement^{12,14,16–19} of the damping of the probe oscillations arising from energy dissipation to the sample yields a noncontact friction coefficient^{20–24} that may be related to the spectrum of field fluctuations at the probe frequency. We adopt here the term noncontact friction to describe the dissipative transfer of energy between macroscopic or mesoscopic bodies that are not, by a reasonable definition, in direct physical contact. For example, the electric force measurements in Ref. 17 probe

interactions between a charged cantilever tip and a polymer thin film that are separated by tens to hundreds of nanometers. Noncontact friction arising from varying mechanisms may be significant in experimental situations that include force microscopy¹⁶ and micromechanics.²⁵ We also consider here the measurement of sample-induced fluctuations in the mechanical resonance frequency of the cantilever probe, which we will refer to later as frequency jitter. These fluctuations in the probe frequency provide a view of lower-frequency dielectric fluctuations.^{26–34}

The first noncontact friction measurements on organic surfaces were performed using an ultrasensitive single-crystal silicon cantilever^{35,36} with a resonant frequency of 7.385 kHz on thin films of polystyrene, poly(methylmethacrylate) (PMMA), and poly(vinyl acetate).^{17,18} The total friction on the capacitatively charged probe tip was decomposed into an intrinsic contribution independent of the sample and a sample-induced noncontact friction. For comparable experimental geometries and at room temperature, the noncontact friction coefficients of these three materials were found to vary by more than an order of magnitude. The noncontact friction was demonstrated to vary quadratically with tip-sample voltage, and hence, with tip charge, consistent with a linear response description in which the friction arises from equilibrium electric field fluctuations unaffected

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by the charged probe. The measured noncontact friction coefficients were shown to agree quantitatively^{17,18} with the predictions of a calculation in which the sample was treated as a dielectric continuum slab of finite thickness, and the friction was determined using linear response theory. Within linear response, the friction is proportional to the Fourier transform at the resonant frequency of the cantilever of the equilibrium correlation function of electric field fluctuations at the location of the probe tip. This correlation function was determined through its relation to the reaction field³⁷ generated by the sample in response to a fictitious time-varying electric dipole placed at the location of the probe. A fictitious electric dipole was chosen because the dipolar energy is linear in field, so that the response function describing the production of the reaction field will involve an electric field autocorrelation function. This reaction field was then calculated within a quasistatic approximation^{4,38,39} to electrodynamics in which the Fourier components of time-varying fields and charge distributions are assumed to obey the static limit of Maxwell's equations. The result relates the noncontact friction to the independently measurable frequency-dependent dielectric function and was shown to describe the relative friction coefficients of the three polymer samples studied¹⁸ as well as the dependence of the noncontact friction coefficient on tip-sample separation.¹⁷

Here we present a unified theoretical treatment of these two observables in electric force microscopy: noncontact friction and frequency jitter. In Sec. II, the cantilever dynamics are described by a Langevin equation,⁴⁰ and the noncontact friction, mean-squared frequency jitter, and jitter power spectrum are related to equilibrium time-correlation functions involving the electric field and its spatial gradient. These time-correlation functions are calculated with a response function approach in Sec. III, where it is shown that the frequency jitter may be related to the reaction field generated in the sample by a fictitious time-dependent electric quadrupole. This treatment yields an expression for the jitter spectral density with the same frequency-dependence predicted by Israeloff and co-workers,^{27,29} but here with explicit forms for all parameters associated with sample identity and experimental geometry. This analysis relies on the quasistatic approximation to electrodynamics.⁴ An alternative and more general approach that circumvents this approximation is presented in Sec. IV, in which a stochastic form of Maxwell's equations is applied to calculate the equilibrium correlation functions of Sec. II. These mesoscopic equations describe fluctuating field variables driven by a stochastic electric polarization that mimics the effect of thermal dynamics in the medium. In a seminal paper on the determination of dispersion forces, Lifshitz^{41,42} used these stochastic Maxwell's equations to calculate the dispersion⁴³ or Casimir^{44,45} force between two macroscopic dielectric bodies. Our fully electrodynamic approach to friction and jitter gives results that reduce to those of Sec. III in the experimentally relevant limit in which the finite time of propagation of radiation between sample and probe may be neglected. This analysis illustrates the connection between electric force microscopy and study of the Casimir force.

The applicability of our model to noncontact friction

FIG. 1. (Color online) To probe electric field fluctuations, a charged cantilever tip oscillates in the x direction at height $z=d$ above the surface of a dielectric sample of thickness h .

measurements has already been demonstrated,^{17,18} but our predictions of the frequency jitter remain to be tested in future experiments. Here we show that the predicted frequency jitter is large enough to permit measurement. Section V describes the laboratory procedures used in Sec. VI to show that the predicted jitter from a PMMA film exceeds the minimum detectable frequency jitter^{13,46} for the apparatus of Refs. 17 and 18. This minimum detectable frequency noise is estimated from measurement of the power spectrum of frequency fluctuations of the cantilever in the absence of a sample together with measurement of the noncontact friction for PMMA.

II. EXPERIMENTAL OBSERVABLES

We consider a cantilever tip with charge q_c located a distance $z=d>0$ above a dielectric slab of thickness h parallel to the xy plane, as shown in Fig. 1. The measurement is carried out at constant tip-sample voltage V_{ts} , so that the tip charge is given by $q_c=CV_{ts}$, with C the capacitance, which is assumed to vary with d as discussed in Sec. VI. The sample is backed by a conductor and is treated as a continuum dielectric, with complex-valued dielectric function $\epsilon(\omega) \equiv \epsilon'(\omega) + i\epsilon''(\omega)$ and dielectric constant $\epsilon'(0)$. The tip oscillates in one dimension parallel to the interface. It is treated as a point charge with x coordinate obeying a Langevin equation⁴⁰

$$\ddot{x}(t) = -\omega_c^2 x(t) - \frac{\gamma}{m} \dot{x}(t) + \frac{q_c}{m} \mathcal{E}_x(x, t), \quad (2.1)$$

with ω_c the resonant frequency of the cantilever in the absence of the sample, γ the noncontact friction coefficient, m the effective mass related to the cantilever force constant k_c

by $m \equiv k_c / \omega_c^2$, and $\mathcal{E}_x(x, t)$ the x component of the fluctuating electric field at the tip. The tip is taken to be harmonic in the absence of any external force and subject to a friction constant rather than a time-dependent friction kernel because the measured tip trajectory $x(t)$ is well described by an underdamped harmonic oscillator with constant friction.^{16,17} The fluctuating electric field in Eq. (2.1) is then written in terms of its average value $E_x(x) \equiv \langle \mathcal{E}_x(x, t) \rangle_{q_c}$, which obeys the conventional macroscopic form of Maxwell's equations, and the fluctuation about this mean, $\delta\mathcal{E}_x(x, t)$,

$$\mathcal{E}_x(x, t) = E_x(x) + \delta\mathcal{E}_x(x, t). \quad (2.2)$$

The angular brackets $\langle \cdots \rangle_{q_c}$ designate a configuration average over all degrees of freedom of the dielectric in the presence of nonzero probe charge q_c . Both mean and fluctuation are then linearized in x about $x=0$,

$$E_x(x) \approx xE_{xx}, \quad (2.3)$$

$$\delta\mathcal{E}_x(x, t) \approx \delta\mathcal{E}_x(t) + x\delta\mathcal{E}_{xx}(t), \quad (2.4)$$

with $E_{xx} \equiv (\partial E_x / \partial x)_{x=0}$ and $\delta\mathcal{E}_{xx}(t) \equiv (\partial \delta\mathcal{E}_x(x, t) / \partial x)_{x=0}$. Within this linearization, Eq. (2.1) becomes a Langevin equation for a Brownian harmonic oscillator with a frequency containing a static field-induced shift $\Delta\omega_c$, as well as a time-varying fluctuation $\delta\omega_c(t)$,

$$\ddot{x}(t) = -\omega_c^2(t)x(t) - \frac{\gamma}{m}\dot{x}(t) + \frac{q_c}{m}\delta\mathcal{E}_x(t), \quad (2.5)$$

$$\omega_c(t) \approx \bar{\omega}_c + \delta\omega_c(t), \quad (2.6)$$

$$\bar{\omega}_c \equiv \omega_c + \Delta\omega_c, \quad (2.7)$$

$$\Delta\omega_c \equiv -\frac{q_c}{2m\omega_c}E_{xx}, \quad (2.8)$$

$$\delta\omega_c(t) \equiv -\frac{q_c}{2m\omega_c}\delta\mathcal{E}_{xx}(t). \quad (2.9)$$

In Eq. (2.6), we have made the experimentally justified¹⁷ assumption that the field-induced frequency shifts are small compared to the resonance frequency.

The friction coefficient in Eq. (2.5) is related to the equilibrium correlation function of electric field fluctuations in the absence of a perturbing charge by a fluctuation-dissipation relation^{16,18}

$$\gamma = \frac{q_c^2}{k_B T} \hat{C}'_{xx}(\omega_c), \quad (2.10)$$

$$C_{xx}(t) \equiv \langle \mathcal{E}_x(t) \mathcal{E}_x(0) \rangle, \quad (2.11)$$

$$\hat{C}_{xx}(\omega) \equiv \int_0^\infty dt e^{i\omega t} C_{xx}(t) = \hat{C}'_{xx}(\omega) + i\hat{C}''_{xx}(\omega). \quad (2.12)$$

In Eq. (2.11), $\langle \cdots \rangle$ denotes the configuration average of the dielectric at $q_c=0$. In this relation, $\delta\mathcal{E}_x$ has been replaced by $\mathcal{E}_x$, since for $q_c=0$, the averaged electric field above the sample vanishes. The one-sided Fourier transform is defined

in Eq. (2.12). We will characterize the frequency jitter by its power spectrum,²⁷⁻³³ $P_{\delta\omega_c}(\omega)$,

$$P_{\delta\omega_c}(\omega) \equiv 4 \int_0^\infty dt \cos \omega t \langle \delta\omega_c(t) \delta\omega_c(0) \rangle, \quad (2.13)$$

$$= \frac{q_c^2}{m^2 \omega_c^2} \hat{C}'_{xx,xx}(\omega), \quad (2.14)$$

$$C_{xx,xx}(t) \equiv \langle \mathcal{E}_{xx}(t) \mathcal{E}_{xx}(0) \rangle, \quad (2.15)$$

and, more simply, by the mean-squared frequency fluctuation

$$\langle (\delta\omega_c)^2 \rangle = \left(\frac{q_c^2}{4m^2 \omega_c^2} \right) C_{xx,xx}(0). \quad (2.16)$$

Calculation of the noncontact friction requires the equilibrium autocorrelation function of electric field fluctuations in Eq. (2.11), while calculation of the statistics of frequency jitter requires the equilibrium autocorrelation function of fluctuations in the electric field gradient in Eq. (2.15). The calculation of these equilibrium correlation functions is addressed in the next two sections.

In the model of Eq. (2.9), frequency jitter reflects fluctuations in the gradient of the electric field in the direction of probe motion. In applying these results to a particular measurement, contributions from other mechanisms for frequency jitter may be considered. The present model takes the probe motion to be purely harmonic in the absence of external forces, which is valid for the cantilever and amplitudes used in Ref. 17, and below in Sec. VI. However, cantilever anharmonicity can induce frequency fluctuations in the same way that anharmonicity of molecular vibrations can result in pure dephasing processes in condensed phases.^{40,47,48} If the harmonic potential of the isolated probe in Eq. (2.1) is augmented by a cubic perturbation $-Ax^3/6$, then the fluctuating probe frequency in Eq. (2.9) gains an additive contribution

$$\delta\omega_c(t) = -\frac{q_c}{2m\omega_c} \delta\mathcal{E}_{xx}(t) + \frac{Aq_c}{2m^2 \omega_c^3} \delta\mathcal{E}_x(t). \quad (2.17)$$

The anharmonicity-induced contribution to the jitter is proportional to the fluctuation in electric field, rather than in field gradient. The jitter correlation function in this picture will involve in addition to the field gradient autocorrelation function considered here, the field correlation function also associated with the noncontact friction in Eq. (2.10) and cross correlations between field and field gradient fluctuations.

Another contribution to the jitter not included here arises from the treatment of the probe dynamics as one-dimensional motion parallel to the interface. A more complete picture treats the cantilever as a pendulum of fixed length,^{35,49,50} whose one-dimensional motion along an arc of a circle includes a component perpendicular to the interface. Treatment of the cantilever as a pendulum with equilibrium orientation perpendicular to the interface modifies the probe frequency fluctuations by an additive term

$$\delta\omega_c(t) = -\frac{q_c}{2m\omega_c}\delta\mathcal{E}_{xx}(t) + \frac{q_c}{2m\omega_c L}\delta\mathcal{E}_z(t), \quad (2.18)$$

with L the length of the pendulum. This second term in Eq. (2.18) introduces coupling of the frequency to field fluctuations in the direction perpendicular to the interface, but becomes small in the limit of a long cantilever. Any tilt in the equilibrium orientation of the cantilever with respect to the interface^{35,49,50} would produce additional contributions to the jitter involving fluctuations in the z gradient of the electric field. In the following development, the contributions to cantilever frequency fluctuations in Eqs. (2.17) and (2.18) from cantilever anharmonicity and cantilever motion along z are assumed to be negligible.

III. FIELD CORRELATION FUNCTIONS FROM RESPONSE THEORY AND THE QUASISTATIC APPROXIMATION

We calculate the field and field gradient autocorrelation functions in Eqs. (2.11) and (2.15) through their connections to response functions. We consider the dielectric to be polarized by a fictitious time-varying charge distribution, producing a reaction electric field⁴ that acts at the location of the charge distribution. This charge distribution is chosen so that a linear response calculation of the reaction field^{4,5,37,39} generated by the dielectric requires a response function related to the sought autocorrelation function. This reaction field is then calculated using the quasistatic approximation to electrodynamics, in which Fourier components of the electric field and charge distribution are assumed to obey the static version of Maxwell's equations.^{4,38} These fictitious charge distributions do not physically represent any aspect of the actual measurement, but are devices in a thought experiment that allow the desired equilibrium correlation function to be calculated from macroscopic electrostatics. The field autocorrelation function $\hat{C}_{xx}(\omega)$ in Eq. (2.12) is determined by considering the polarization of the dielectric by a time-varying electric dipole, since the electric dipole moment couples to the electric field in the Hamiltonian. The field gradient autocorrelation function $\hat{C}_{xx,xx}(\omega)$ is calculated by treating the interaction of the dielectric with a time-varying electric quadrupole, since this quantity couples to electric field gradients in the Hamiltonian.

To compute the coefficient of noncontact friction, we consider a fictitious electric dipole $\mu(t)$, oriented along x , and located at $z=d>0$, interacting with the dielectric according to the perturbation Hamiltonian

$$H_{\text{int}}(t) = -\mu(t)\mathcal{E}_x. \quad (3.1)$$

Classical mechanical linear response theory relates the x component of the reaction field to the field autocorrelation function through the response function $\hat{\Phi}_\mu(\omega)$,

$$\hat{E}_x(\omega) = \hat{\mu}(\omega)\hat{\Phi}_\mu(\omega), \quad (3.2)$$

$$\hat{\Phi}_\mu(\omega) \equiv [i\omega\hat{C}_{xx}(\omega) + C_{xx}(0)]/(k_B T). \quad (3.3)$$

The macroscopic electric field E_x obeys the conventional form of Maxwell's equations and is related to the micro-

scopic, fluctuating field $\mathcal{E}_x$ in Eq. (3.1) by $E_x = \langle \mathcal{E}_x \rangle$, with the brackets denoting an average over the degrees of freedom of the dielectric. The cosine transform of the field correlation function, related to the friction in Eq. (2.10), is then

$$\hat{C}'_{xx}(\omega) = \left(\frac{k_B T}{\omega} \right) \hat{\Phi}''_\mu(\omega). \quad (3.4)$$

The response function is obtained by solving the quasistatic limit of Maxwell's equations

$$\nabla \times \hat{\mathbf{E}}(\omega) = 0, \quad (3.5)$$

$$\epsilon(\omega) \nabla \cdot \hat{\mathbf{E}}(\omega) = 4\pi\hat{\rho}(\omega), \quad (3.6)$$

with $\epsilon(\omega)$ the complex-valued dielectric function and $\hat{\rho}(\omega)$ the charge density, subject to the boundary conditions of continuity across the interface of the component of the electric displacement $\epsilon(\omega)\hat{\mathbf{E}}(\omega)$ perpendicular to the interface and of the component of $\hat{\mathbf{E}}(\omega)$ parallel to the interface. This boundary value problem may be solved, for example, by the method of images¹⁸

$$\hat{\Phi}_\mu(\omega) = \frac{\zeta(\omega)}{2d^3} I_2(\omega), \quad (3.7)$$

$$I_n(\omega) \equiv \int_0^\infty dq q^n e^{-2q} \left[\frac{1 - e^{-4q(h/d)}}{1 + \zeta(\omega)e^{-2q(h/d)}} \right], \quad (3.8)$$

$$\zeta(\omega) \equiv \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 1}. \quad (3.9)$$

Substitution of this result for the response function in Eq. (3.4) for the field autocorrelation function gives

$$\hat{C}'_{xx}(\omega) = \frac{k_B T \zeta''(\omega)}{2\omega d^3} J_2(\omega), \quad (3.10)$$

$$J_n(\omega) \equiv \int_0^\infty dq q^n e^{-2q} \times \left\{ \frac{1 - e^{-4q(h/d)}}{(1 + \zeta'(\omega)e^{-2q(h/d)})^2 + [\zeta''(\omega)]^2 e^{-4q(h/d)}} \right\}. \quad (3.11)$$

In the limit of infinite dielectric thickness $h \gg d$, the integral in Eq. (3.11) may be performed analytically, and the field autocorrelation function varies as d^{-3} ,

$$\hat{C}'_{xx}(\omega) \approx \left(\frac{k_B T}{4\omega d^3} \right) \left[\frac{\epsilon''(\omega)}{|\epsilon(\omega) + 1|^2} \right]. \quad (3.12)$$

For finite sample thickness, additional d dependence results from the integral in Eq. (3.11). The noncontact friction for arbitrary h/d follows from substituting Eq. (3.10) into Eq. (2.10),^{17,18}

$$\gamma = \frac{q_c^2 \zeta''(\omega_c)}{2\omega_c d^3} J_2(\omega_c). \quad (3.13)$$

This relation connects γ to the tip charge, sample dielectric function and thickness, and tip-sample separation.

We next apply this response function strategy to calculate the autocorrelation function of field gradient fluctuations. A fictitious time-varying electric quadrupole is located a distance $d > 0$ from the interface. The quadrupole tensor is diagonal in the Cartesian basis of Fig. 1, with nonzero quadrupole tensor elements $Q_{xx} \equiv Q(t)$, $Q_{yy} = Q_{zz} = -Q(t)/2$. This charge distribution may be visualized, for example, as a central charge of magnitude $-2q(t)$ with two charges of magnitude $q(t)$ displaced from the central charge along x by $\pm r$, in the limit $r \rightarrow 0$ with $4q(t)r^2 = Q(t)$. The orientation of this charge distribution is chosen for convenience, in that rotating this quadrupole would not alter the final results obtained later. The interaction between quadrupole and medium is specified by the Hamiltonian

$$H_{\text{int}}(t) = -\frac{Q(t)}{6} \left[\frac{\partial \mathcal{E}_x}{\partial x} - \left(\frac{1}{2} \right) \frac{\partial \mathcal{E}_y}{\partial y} - \left(\frac{1}{2} \right) \frac{\partial \mathcal{E}_z}{\partial z} \right]. \quad (3.14)$$

The analog of Eqs. (3.2) and (3.3) relating macroscopic field gradients to response functions $\hat{\Phi}_Q^\alpha(\omega)$ and then to correlation functions of fluctuating field gradients is

$$\hat{E}_{\alpha\alpha}(\omega) = \hat{Q}(\omega) \hat{\Phi}_Q^\alpha(\omega), \quad (3.15)$$

$$\begin{aligned} \hat{\Phi}_Q^\alpha(\omega) = \frac{1}{6k_B T} \Big\{ i\omega \hat{C}_{\alpha\alpha,xx}(\omega) + C_{\alpha\alpha,xx}(0) - \frac{1}{2} [i\omega \hat{C}_{\alpha\alpha,yy}(\omega) \\ + C_{\alpha\alpha,yy}(0)] - \frac{1}{2} [i\omega \hat{C}_{\alpha\alpha,zz}(\omega) + C_{\alpha\alpha,zz}(0)] \Big\}, \end{aligned} \quad (3.16)$$

with $\alpha = x, y, z$ and $C_{\alpha\alpha,\beta\beta}(t) \equiv \langle [\partial \mathcal{E}_\alpha(t) / \partial \alpha] [\partial \mathcal{E}_\beta(0) / \partial \beta] \rangle$. Solving the quasistatic version of Maxwell's equations in Eqs. (3.5) and (3.6) for these field gradients gives

$$\hat{\Phi}_Q^x(\omega) = \frac{9}{4} R(\omega), \quad (3.17)$$

$$\hat{\Phi}_Q^y(\omega) = \frac{3}{4} R(\omega), \quad (3.18)$$

$$\hat{\Phi}_Q^z(\omega) = -3R(\omega), \quad (3.19)$$

$$R(\omega) \equiv \frac{\zeta(\omega)}{24d^5} I_4(\omega). \quad (3.20)$$

The integral $I_4(\omega)$ is defined in Eq. (3.8). Equations (3.17)–(3.19) necessarily satisfy $\sum_\alpha \hat{\Phi}_Q^\alpha(\omega) = 0$, which follows from $\nabla \cdot \hat{\mathbf{E}}(\omega) = 0$.

The jitter power spectrum in Eq. (2.14) is proportional to the cosine transform $\hat{C}'_{xx,xx}(\omega)$. Taking the imaginary parts of Eqs. (3.17)–(3.19) relates cosine transforms of various field gradient correlation functions to the imaginary part of $R(\omega)$ in Eq. (3.20),

$$\left(\frac{27k_B T}{2\omega} \right) R'' = \hat{C}'_{xx,xx} - \frac{1}{2} \hat{C}'_{xx,yy} - \frac{1}{2} \hat{C}'_{xx,zz}, \quad (3.21)$$

$$\left(\frac{9k_B T}{2\omega} \right) R'' = \hat{C}'_{yy,xx} - \frac{1}{2} \hat{C}'_{yy,yy} - \frac{1}{2} \hat{C}'_{yy,zz}, \quad (3.22)$$

$$\left(\frac{18k_B T}{\omega} \right) R'' = \frac{1}{2} \hat{C}'_{zz,yy} - \hat{C}'_{zz,xx} + \frac{1}{2} \hat{C}'_{zz,zz}. \quad (3.23)$$

These field gradient correlation functions are not all distinct. From classical mechanical time-reversal symmetry, $\hat{C}'_{\alpha\alpha,\beta\beta}(\omega) = \hat{C}'_{\beta\beta,\alpha\alpha}(\omega)$ and from the isotropy of this particular problem in the xy plane, $\hat{C}'_{xx,xx}(\omega) = \hat{C}'_{yy,yy}(\omega)$ and $\hat{C}'_{xx,zz}(\omega) = \hat{C}'_{yy,zz}(\omega)$. With these equalities, Eqs. (3.22) and (3.23) become

$$\left(\frac{9k_B T}{2\omega} \right) R'' = \hat{C}'_{xx,yy} - \frac{1}{2} \hat{C}'_{xx,xx} - \frac{1}{2} \hat{C}'_{xx,zz}, \quad (3.24)$$

$$\left(\frac{18k_B T}{\omega} \right) R'' = \frac{1}{2} (\hat{C}'_{zz,zz} - \hat{C}'_{xx,zz}), \quad (3.25)$$

so that Eqs. (3.21), (3.24), and (3.25) represent three constraints for four unknown correlation functions.

The fourth constraint required to determine $\hat{C}'_{xx,xx}(\omega)$ is constructed by applying the quasistatic version of Maxwell's equations to the mesoscopic fluctuating field $\mathcal{E}$ rather than the macroscopic averaged field $\mathbf{E}$ in Eqs. (3.5) and (3.6). In the Maxwell's equations obeyed by $\mathbf{E}$, the dielectric medium is represented by its dielectric function $\epsilon(\omega)$, while in the Maxwell's equations obeyed by $\mathcal{E}$, the medium is represented microscopically as a time-varying charge distribution. In vacuum, the fluctuating field satisfies $\nabla \cdot \mathcal{E}(t) = 0$, so that for $z > 0$,

$$\begin{aligned} \langle [\nabla \cdot \mathcal{E}(t)] [\nabla \cdot \mathcal{E}(0)] \rangle = 2C_{xx,xx}(t) + C_{zz,zz}(t) + 4C_{xx,zz}(t) \\ + 2C_{xx,yy}(t) = 0. \end{aligned} \quad (3.26)$$

Taking Fourier transforms yields

$$\hat{C}'_{xx,xx} + \frac{1}{2} \hat{C}'_{zz,zz} + 2\hat{C}'_{xx,zz} + \hat{C}'_{xx,yy} = 0. \quad (3.27)$$

Equations (3.21), (3.24), (3.25), and (3.27) provide four independent constraints for four field gradient correlation functions and can be solved for the desired $\hat{C}'_{xx,xx}(\omega)$,

$$\hat{C}'_{xx,xx}(\omega) = \frac{3k_B T \zeta''(\omega)}{8\omega d^5} J_4(\omega). \quad (3.28)$$

The integral $J_4(\omega)$ is defined in Eq. (3.11). As with Eq. (3.10) for the field autocorrelation function, Eq. (3.28) simplifies in the limit of an infinitely thick sample, $h/d \gg 1$,

$$\hat{C}'_{xx,xx}(\omega) = \left(\frac{9k_B T}{16\omega d^5} \right) \left[\frac{\epsilon''(\omega)}{|\epsilon(\omega) + 1|^2} \right]. \quad (3.29)$$

The jitter power spectrum for general h/d may then be determined from Eq. (2.14),

$$P_{\delta\omega_c}(\omega) = \frac{3q_c^2 k_B T \zeta''(\omega)}{8m^2 \omega_c^2 \omega d^5} J_4(\omega). \quad (3.30)$$

In the limit of low frequency,^{28–30} $\epsilon''(\omega) \ll \epsilon'(\omega) \approx \epsilon'(0)$, the power spectrum in Eq. (3.30) factors into a product of a function of frequency and a function of tip-sample separation and sample thickness

$$P_{\delta\omega_c}(\omega) \approx \frac{3q_c^2 k_B T J_4(0)}{4m^2 \omega_c^2 d^5 [\epsilon'(0) + 1]^2} \left[\frac{\epsilon''(\omega)}{\omega} \right]. \quad (3.31)$$

Frequency jitter may also be more simply characterized by the mean-squared frequency fluctuation in Eq. (2.16). The zero-time limit of the field gradient correlation function may be obtained by the static analog of the strategy that produced Eqs. (3.21), (3.24), (3.25), and (3.27). The static analogs of these relations may be obtained with the substitutions $\hat{C}'_{\alpha\alpha,\beta\beta}(\omega) \rightarrow C_{\alpha\alpha,\beta\beta}(0)$ and $R''(\omega)/\omega \rightarrow R(0)$. The mean-squared frequency fluctuation is then given by

$$\langle (\delta\omega_c)^2 \rangle = \frac{3q_c^2 k_B T \zeta(0)}{32m^2 \omega_c^2 d^5} I_4(0), \quad (3.32)$$

with $I_4(0)$ the integral in Eq. (3.8) with $n=4$ and with $\epsilon(\omega)$ set to $\epsilon'(0)$. The mean-squared frequency fluctuation depends on the dielectric constant $\epsilon'(0)$, through $\zeta(0)$, defined as the zero frequency limit of Eq. (3.9).

The power spectrum of the frequency jitter induced by a dielectric on an oscillating charged probe has been measured by Israeloff and co-workers^{27–29} and analyzed with the form

$$P_{\delta\omega_c}(\omega) = \left(\frac{\partial \bar{\omega}_c}{\partial V_{ts}} \right)^2 (4C_0 G) \left[\frac{k_B T \epsilon''(\omega)}{\omega C^2} \right], \quad (3.33)$$

with C and C_0 , respectively, the capacitance with and without the dielectric sample. G is a dimensionless factor that is stated^{27–29} to depend on experimental geometry and on the dielectric constant of the sample. Like our limiting expression for $\omega \rightarrow 0$ in Eq. (3.31), Eq. (3.33) factors into a product of a function of ω and a function depending on dielectric constant and geometry. The two expressions predict the same ω dependence: $\epsilon''(\omega)/\omega$. To compare the frequency-independent factors in Eqs. (3.33) and (3.31) we must determine the voltage derivative of the mean probe frequency appearing in Eq. (3.33). The static, sample-induced shift in the probe frequency is related in Eq. (2.8) to the averaged field gradient E_{xx} . Solving the same electrostatics boundary value problem that led to Eq. (3.32) gives

$$E_{xx} = -\frac{\zeta(0)q_c}{2d^3} I_2(0), \quad (3.34)$$

with $I_2(\omega)$ defined in Eq. (3.8). The tip charge q_c is then proportional to the voltage derivative of the frequency in Eq. (2.8), according to

$$q_c = \left(\frac{\partial \bar{\omega}_c}{\partial V_{ts}} \right) \frac{2m\omega_c d^3}{\zeta(0)I_2(0)C}. \quad (3.35)$$

Substitution of this result into our limiting expression for $P_{\delta\omega_c}(\omega)$ in Eq. (3.31) gives

$$P_{\delta\omega_c}(\omega) = \left(\frac{\partial \bar{\omega}_c}{\partial V_{ts}} \right)^2 \left\{ \frac{3dJ_4(0)}{[\zeta(0)I_2(0)[\epsilon'(0) + 1]^2]} \right\} \times \left[\frac{k_B T \epsilon''(\omega)}{\omega C^2} \right]. \quad (3.36)$$

Comparison of our limiting Eq. (3.36) to Eq. (3.33) shows that the two relations predict the same frequency dependence for $P_{\delta\omega_c}(\omega)$, with Eq. (3.36) providing explicit dependence

on dielectric constant, sample thickness, and tip-sample separation.

The experiments of Israeloff and co-workers in Refs. 27–29 employed a configuration in which the probe oscillates perpendicular to the interface, in the z direction of Fig. 1. All results for noncontact friction and frequency jitter presented here are derived for the geometry used in our Refs. 17 and 18, in which the probe moves parallel to the interface, in the x direction of Fig. 1. The noncontact friction coefficient and the jitter power spectrum for the case of motion along z may be readily derived with the methods of this section. For example, the jitter power spectrum in Eqs. (2.13) and (2.14) for this case is proportional to the Fourier transform of the autocorrelation function of the z derivative of the z component of the electric field fluctuation $\hat{C}'_{zz,zz}(\omega)$. This quantity may be determined by solving Eqs. (3.21), (3.24), (3.25), and (3.27) to yield a result that differs from Eq. (3.28) only by a numerical factor: $\hat{C}'_{zz,zz}(\omega) = \frac{8}{3} \hat{C}'_{xx,xx}(\omega)$. Thus, for a hypothetical experiment carried out at constant tip charge and with a probe amplitude small compared to the tip-sample separation, the present dielectric continuum model predicts jitter power spectra for the two geometries that differ only by this numerical factor, and the coefficients of noncontact friction may similarly be shown to differ only by a numerical factor. A complete analysis for the experimentally relevant case of a constant-voltage probe oscillating with a non-negligible amplitude along z , which will not be considered further here, would need to account for both an additional time variation in the electric field at the tip and a time variation in the magnitude of the tip charge.

IV. FIELD CORRELATION FUNCTIONS FROM STOCHASTIC ELECTRODYNAMICS

In the previous section, we calculated autocorrelation functions of electric field and electric field gradient fluctuations by determining the response functions associated with the reaction fields induced by fictitious time-varying charge distributions. These reaction fields were then determined with a quasistatic approximation to electrodynamics. Here we determine these two correlation functions with an alternative strategy based on a full electrodynamic description. We apply the stochastic form of Maxwell's equations used by Lifshitz^{22,41,42,51} to determine the dispersion force^{43,45} between two semi-infinite dielectric slabs to calculate the correlation functions directly in the absence of external charge distributions. To simplify this more general analysis, we treat the limit of infinite sample thickness $h \rightarrow \infty$ as in Eqs. (3.12) and (3.29).

For nonmagnetic media, the stochastic Maxwell's equations are^{41,42,51}

$$\nabla \times \tilde{\mathcal{E}}(\mathbf{r}, \omega) = ik\tilde{\mathcal{H}}(\mathbf{r}, \omega), \quad (4.1)$$

$$\nabla \times \tilde{\mathcal{H}}(\mathbf{r}, \omega) = -ik\epsilon\tilde{\mathcal{E}}(\mathbf{r}, \omega) - ik\tilde{\mathcal{P}}(\mathbf{r}, \omega), \quad (4.2)$$

$$k \equiv \omega/c. \quad (4.3)$$

In Eq. (4.2) and below, we abbreviate the complex-valued dielectric function by $\epsilon(\omega) \rightarrow \epsilon$. The fluctuating electric and

magnetic fields are denoted $\tilde{\mathcal{E}}$ and $\tilde{\mathcal{H}}$, with $\tilde{\mathcal{P}}/4\pi$ representing the fluctuating electric polarization of the dielectric. Frequency-dependent quantities in Eqs. (4.1) and (4.2) are double-sided Fourier transforms, distinct from the single-sided Fourier-Laplace transform in Eq. (2.12). The spatial Fourier transform of $\tilde{\mathcal{P}}(\mathbf{r}, \omega)$ denoted $\mathcal{P}(\mathbf{q}, \omega)$ is defined by

$$\tilde{\mathcal{P}}(\mathbf{r}, \omega) = \int d\mathbf{q} e^{i\mathbf{q}_{\parallel} \cdot \mathbf{r}} \cos q_z z \mathcal{P}(\mathbf{q}, \omega), \quad (4.4)$$

with $\mathbf{q}_{\parallel}$ the projection of the Fourier vector $\mathbf{q}$ parallel to the interface and q_z the component perpendicular to the interface. The fluctuating polarization has zero mean and a correlation function^{41,42}

$$\langle \mathcal{P}_{\alpha}(\bar{\mathbf{q}}, \bar{\omega}) \mathcal{P}_{\beta}(\mathbf{q}, \omega) \rangle = \delta_{\alpha\beta} \delta(\mathbf{q} + \bar{\mathbf{q}}) \delta(\omega + \bar{\omega}) \left[\frac{\epsilon''(\omega) k_B T}{\pi^3 \omega} \right]. \quad (4.5)$$

Equation (4.5) is the classical mechanical limit of the relation employed by Lifshitz.^{41,42} For the description of room-temperature measurements and frequencies of kHz or less, the assumption $k_B T \gg \hbar \omega$ is entirely justified. According to Eq. (4.5), the fluctuating polarization vector is delta correlated in space and uncorrelated in orientation with a correlation function having frequency dependence associated with the absorptive part of the dielectric function.

We follow Lifshitz⁴¹ by postulating the following forms for the electric field within the dielectric for $z < 0$, $\tilde{\mathcal{E}}^{(-)}(\mathbf{r}, \omega)$ and outside the dielectric for $z > 0$, $\tilde{\mathcal{E}}^{(+)}(\mathbf{r}, \omega)$,

$$\begin{aligned} \tilde{\mathcal{E}}^{(-)}(\mathbf{r}, \omega) = & \int d\mathbf{q} e^{i\mathbf{q}_{\parallel} \cdot \mathbf{r}} [\mathcal{C}(\mathbf{q}, \omega) \cos q_z z + i\mathcal{S}(\mathbf{q}, \omega) \sin q_z z] \\ & + \int d\mathbf{q}_{\parallel} \mathcal{R}(\mathbf{q}_{\parallel}, \omega) e^{i\mathbf{q}_{\parallel} \cdot \mathbf{r} - isz}, \end{aligned} \quad (4.6)$$

$$s \equiv \sqrt{\epsilon k^2 - q_{\parallel}^2}, \quad (4.7)$$

$$\tilde{\mathcal{E}}^{(+)}(\mathbf{r}, \omega) = \int d\mathbf{q}_{\parallel} e^{i\mathbf{q}_{\parallel} \cdot \mathbf{r} + ipz} \mathcal{T}(\mathbf{q}_{\parallel}, \omega), \quad (4.8)$$

$$p \equiv \sqrt{k^2 - q_{\parallel}^2}. \quad (4.9)$$

The Fourier components $\mathcal{C}$ and $\mathcal{S}$ are associated with the electric field generated within the dielectric by the fluctuating polarization, while $\mathcal{R}$ describes waves reflected back into the medium at the interface with vacuum. Waves transmitted from the medium into the vacuum have Fourier component $\mathcal{T}$. The wave vector s associated with the propagation of the reflected waves is complex valued, and the wave vector p associated with the transmitted waves is either purely real or purely imaginary, with the latter representing evanescent waves. The square root in Eq. (4.7) must be taken so that the imaginary part of s is positive, as required by Eq. (4.6). The square root in Eq. (4.9) must similarly be taken so that the imaginary part of p is positive, as required in Eq. (4.8). The components $\mathcal{C}$ and $\mathcal{S}$ are calculated by solving Eqs. (4.1) and (4.2) in an infinite dielectric medium, and the reflected and transmitted components $\mathcal{R}$ and $\mathcal{T}$ are deter-

mined by satisfying boundary conditions at the interface. Lifshitz has determined⁴¹ that

$$\begin{aligned} \mathcal{C}(\mathbf{q}, \omega) = & \left[\frac{1}{\epsilon(q_z^2 - s^2)} \right] \{ \epsilon k^2 \mathcal{P}(\mathbf{q}, \omega) - [\mathbf{q}_{\parallel} \cdot \mathcal{P}(\mathbf{q}, \omega)] \mathbf{q}_{\parallel} \\ & - q_z^2 \mathcal{P}_z(\mathbf{q}, \omega) \hat{\mathbf{z}} \}, \end{aligned} \quad (4.10)$$

$$\mathcal{S}(\mathbf{q}, \omega) = - \left[\frac{q_z}{\epsilon(q_z^2 - s^2)} \right] \{ [\mathbf{q}_{\parallel} \cdot \mathcal{P}(\mathbf{q}, \omega)] \hat{\mathbf{z}} + \mathcal{P}_z(\mathbf{q}, \omega) \mathbf{q}_{\parallel} \}. \quad (4.11)$$

The form of the fluctuating magnetic field can be obtained by substituting Eqs. (4.6) and (4.8) into Eqs. (4.1) and (4.2).

To formulate the boundary conditions, we define the following projections of any vector $\mathbf{A}$. The projection parallel to the interface is $\mathbf{A}_{\parallel} \equiv \mathbf{A} - A_z \hat{\mathbf{z}}$. The component of $\mathbf{A}_{\parallel}$ along $\mathbf{q}_{\parallel}$ is $A_q \equiv \mathbf{A}_{\parallel} \cdot \mathbf{q}_{\parallel} / q_{\parallel}$. The component of $\mathbf{A}_{\parallel}$ perpendicular to $\mathbf{q}_{\parallel}$ is $A_n \equiv \mathbf{A}_{\parallel} - A_q$. The continuity of $\mathcal{E}_{\parallel}$ at the interface yields the pair of scalar relations

$$\mathcal{T}_q(\mathbf{q}_{\parallel}, \omega) = \mathcal{R}_q(\mathbf{q}_{\parallel}, \omega) + \int_{-\infty}^{\infty} dq_z \mathcal{C}_q(\mathbf{q}, \omega), \quad (4.12)$$

$$\mathcal{T}_n(\mathbf{q}_{\parallel}, \omega) = \mathcal{R}_n(\mathbf{q}_{\parallel}, \omega) + \int_{-\infty}^{\infty} dq_z \mathcal{C}_n(\mathbf{q}, \omega), \quad (4.13)$$

and the continuity of $\mathcal{H}_{\parallel}$ implies the relations

$$\begin{aligned} \mathcal{R}_z(\mathbf{q}_{\parallel}, \omega) q_{\parallel} + s \mathcal{R}_q(\mathbf{q}_{\parallel}, \omega) + \int_{-\infty}^{\infty} dq_z [\mathcal{C}_z(\mathbf{q}_{\parallel}, \omega) q_{\parallel} - q_z \mathcal{S}_q(\mathbf{q}, \omega)] \\ = \mathcal{T}_z(\mathbf{q}_{\parallel}, \omega) q_{\parallel} - p \mathcal{T}_q(\mathbf{q}_{\parallel}, \omega), \end{aligned} \quad (4.14)$$

$$s \mathcal{R}_n(\mathbf{q}_{\parallel}, \omega) - \int_{-\infty}^{\infty} dq_z q_z \mathcal{S}_n(\mathbf{q}, \omega) = -p \mathcal{T}_n(\mathbf{q}_{\parallel}, \omega). \quad (4.15)$$

In addition, the requirements that the reflected wave in the dielectric and the transmitted wave in the vacuum be transverse imply the scalar relations

$$q_{\parallel} \mathcal{R}_q(\mathbf{q}_{\parallel}, \omega) - s \mathcal{R}_z(\mathbf{q}_{\parallel}, \omega) = 0, \quad (4.16)$$

$$q_{\parallel} \mathcal{T}_q(\mathbf{q}_{\parallel}, \omega) + p \mathcal{T}_z(\mathbf{q}_{\parallel}, \omega) = 0. \quad (4.17)$$

Equations (4.12)–(4.17) give six scalar constraints for the six spatial components of the vectors $\mathcal{R}$ and $\mathcal{T}$. Solving these constraints for the components of the transmitted wave parallel to the plane of the interface gives

$$\mathcal{T}_n(\mathbf{q}_{\parallel}, \omega) = \left(\frac{sk^2}{s+p} \right) \int_{-\infty}^{\infty} \frac{dq_z}{q_z^2 - s^2} \mathcal{P}_n(\mathbf{q}, \omega), \quad (4.18)$$

$$\mathcal{T}_q(\mathbf{q}_{\parallel}, \omega) = \left(\frac{sp}{s+\epsilon p} \right) \int_{-\infty}^{\infty} \frac{dq_z}{q_z^2 - s^2} [s \mathcal{P}_q(\mathbf{q}, \omega) - q_{\parallel} \mathcal{P}_z(\mathbf{q}, \omega)]. \quad (4.19)$$

The x component of the fluctuating electric field in the vacuum is related to the three spatial components of the fluctuating polarization in the dielectric by

$$\begin{aligned}
\tilde{\mathcal{E}}_x^{(+)}(\mathbf{r}, \omega) = & \int d\mathbf{q}_{\parallel} e^{i(pz + \mathbf{q}_{\parallel} \cdot \mathbf{r})} \int_{-\infty}^{\infty} \frac{dq_z}{q_z^2 - s^2} \left\{ \mathcal{P}_x(\mathbf{q}, \omega) \right. \\
& \times \left[\left(\frac{s^2 p}{s + \epsilon p} \right) \cos^2 \phi + \left(\frac{sk^2}{s + p} \right) \sin^2 \phi \right] \\
& + \mathcal{P}_y(\mathbf{q}, \omega) \cos \phi \sin \phi \left[\left(\frac{s^2 p}{s + \epsilon p} \right) - \left(\frac{sk^2}{s + p} \right) \right] \\
& \left. - \mathcal{P}_z(\mathbf{q}, \omega) \left(\frac{spq_{\parallel}}{s + \epsilon p} \right) \cos \phi \right\}, \quad (4.20)
\end{aligned}$$

with ϕ specifying the orientation of $\mathbf{q}_{\parallel}$ relative to x .

The autocorrelation function of this temporal Fourier component of the electric field is related to the cosine transform of the electric field correlation function in Eq. (2.12) by

$$\langle \tilde{\mathcal{E}}_x^{(+)}(\mathbf{r}, \omega) \tilde{\mathcal{E}}_x^{(+)}(\mathbf{r}, \bar{\omega}) \rangle = \pi^{-1} \delta(\omega + \bar{\omega}) \hat{C}'_{xx}(\omega). \quad (4.21)$$

Substituting Eq. (4.20) into Eq. (4.21) and applying the delta function in the wave vector in Eq. (4.5) permits one three-dimensional integration over the wave vector to be performed. The condition $\bar{\omega} = -\omega$ imposed by the delta function in frequency in Eq. (4.5) causes $\epsilon(\bar{\omega}) \rightarrow \epsilon(-\omega) = \epsilon^*(\omega)$.⁴² The constraints $\bar{\omega} = -\omega$ and $\bar{\mathbf{q}} = -\mathbf{q}$ do not affect the wave vector of the transmitted wave in Eq. (4.9), i.e., $p(\bar{\omega}, \bar{q}_{\parallel}) = p(-\omega, q_{\parallel}) = p(\omega, q_{\parallel})$, but alter the value of the complex-valued wave vector of the reflected wave s in Eq. (4.7) $s(\bar{\omega}, \bar{q}_{\parallel}, \epsilon(\bar{\omega})) = s(\omega, q_{\parallel}, \epsilon^*) = -s^*(\omega, q_{\parallel}, \epsilon)$. The negative sign in the last equality follows from the requirement in Eq. (4.6) that the imaginary part of s be positive. The integral over q_z that results from substituting the expression in Eq. (4.20) into Eq. (4.21) can be carried out analytically⁴¹

$$\int_{-\infty}^{\infty} \frac{dq_z}{|q_z^2 - s^2|^2} = \frac{\pi s'}{k^2 \epsilon''(\omega) |s|^2}. \quad (4.22)$$

Integration over the orientation of $\mathbf{q}_{\parallel}$ in Eq. (4.20) gives $\hat{C}'_{xx}(\omega)$ as a one-dimensional integral over the magnitude of this wave vector

$$\begin{aligned}
\hat{C}'_{xx}(\omega) = & \left(\frac{k_B T}{\omega} \right) \int_0^{\infty} dq_{\parallel} q_{\parallel} s' e^{2ipz} \\
& \times \left\{ \frac{(|s|^2 + q_{\parallel}^2) p^2 k^{-2}}{(\epsilon p + s)(\epsilon^* p - s^*)} - \frac{k^2}{(p + s)(p - s^*)} \right\}. \quad (4.23)
\end{aligned}$$

We follow Lifshitz by changing integration variables from the magnitude of the wave vector in the xy plane, $q_{\parallel}$, to the magnitude of the z component of the wave vector of the transmitted wave, p , in Eq. (4.9). According to Eq. (4.9), as the real-valued $q_{\parallel}$ varies from 0 to k , p runs over real numbers from k to 0, and as $q_{\parallel}$ varies from k to ∞ , p takes on purely imaginary values from $i0$ to $i\infty$. The integral over real-valued p contains contributions from undamped propagating waves emitted by the sample and vanishes in the quasistatic limit $k \rightarrow 0$. We consider here only the integral over imaginary-valued p , which represents contributions from the

evanescent waves that give rise to the Casimir force.⁴¹ With $\eta \equiv -ipz$ for imaginary p and with $\kappa \equiv kz$, the integral over purely imaginary p in Eq. (4.23) becomes

$$\begin{aligned}
\hat{C}'_{xx}(\omega) = & \left(\frac{k_B T}{\omega z^3} \right) \int_0^{\infty} d\eta \eta e^{-2\eta w'} \\
& \times \left[\frac{(\eta^2 + \kappa^2 + |w|^2) \eta^2 \kappa^{-2}}{|w + i\epsilon\eta|^2} + \frac{\kappa^2}{|w + i\eta|^2} \right], \quad (4.24)
\end{aligned}$$

$$w \equiv \sqrt{(\epsilon - 1)\kappa^2 - \eta^2}. \quad (4.25)$$

The square root in Eq. (4.25) should be taken so that $w' > 0$. The expression in Eq. (4.24) depends on the speed of light through its dependence on κ and depends on tip-sample separation z both through this κ dependence and through an explicit prefactor of z^{-3} . In the limit $\kappa = \omega z/c \rightarrow 0$, in which propagation effects are negligible, the complex-valued wave vector w in Eq. (4.25) associated with the reflected wave in the dielectric becomes $w \rightarrow \kappa^2 \epsilon' / 2\eta + i\eta$. Substituting this limit into Eq. (4.24), performing the integral over η , and setting $z = d$ gives Eq. (3.12), obtained previously by calculating the reaction field induced by a time-varying dipole using a quasistatic approximation to electrodynamics. Evaluation of Eq. (4.24) for nonzero κ provides corrections to this limiting expression associated with the finite speed of light. For the experiments of Ref. 17, these corrections are not expected to be numerically significant. For a frequency of 7 kHz and a tip-sample separation $d = 100$ nm, $\kappa = \omega d/c$ is of order 10^{-11} .

The power spectrum of the frequency jitter is related to the cosine transform of the autocorrelation function of fluctuations in the electric field gradient in Eq. (2.14). The field gradient is obtained by performing the derivative $(\partial/\partial x) \exp(i\mathbf{q}_{\parallel} \cdot \mathbf{r})$ in Eq. (4.20). The field gradient correlation function follows from analogous manipulations to those producing Eq. (4.23),

$$\begin{aligned}
\hat{C}'_{xx,xx}(\omega) = & \left(\frac{k_B T}{4\omega} \right) \int_0^{\infty} dq_{\parallel} q_{\parallel}^3 s' e^{2ipz} \\
& \times \left[\frac{3(|s|^2 + q_{\parallel}^2) p^2 k^{-2}}{(\epsilon p + s)(\epsilon^* p - s^*)} - \frac{k^2}{(p + s)(p - s^*)} \right]. \quad (4.26)
\end{aligned}$$

Changing integration variables from $q_{\parallel}$ to p and retaining the integration over evanescent waves with purely imaginary p as in Eq. (4.24) gives

$$\begin{aligned}
\hat{C}'_{xx,xx}(\omega) = & \left(\frac{k_B T}{4\omega z^5} \right) \int_0^{\infty} d\eta \eta (\kappa^2 + \eta^2) e^{-2\eta w'} \\
& \times \left[\frac{3(\eta^2 + \kappa^2 + |w|^2) \eta^2 \kappa^{-2}}{|w + i\epsilon\eta|^2} + \frac{\kappa^2}{|w + i\eta|^2} \right]. \quad (4.27)
\end{aligned}$$

In the limit $\kappa \rightarrow 0$, Eq. (4.27) with $z = d$ recovers the expression calculated in Eq. (3.29) from a quasistatic determination of the reaction field induced by a time-varying electric quadrupole.

In this section and in the preceding one, we have shown that identical expressions for the electric field and electric field gradient correlation functions may be obtained by solving the macroscopic Maxwell's equations with a quasistatic approximation made at the level of the equations themselves and from solving a stochastic version of Maxwell's equations and taking the quasistatic limit $c \rightarrow \infty$ at the level of the solution. The direct calculation of the fluctuating electric field as in Eq. (4.20) has advantages over the approach presented in Sec. III, even if the quasistatic limit is taken. The linear response method of Sec. III requires that a distinct electrostatics problem be solved for each correlation function to be calculated. The calculation of the field correlation function required consideration of a dielectric polarized by an external electric dipole, while the evaluation of the field gradient correlation function required a new calculation for a dielectric polarized by an external quadrupole. By contrast, with the method of this section, once the field has been calculated as in Eq. (4.20), any correlation function involving the field or its spatial derivatives may then be determined. In the present work, the cantilever tip was represented by a point charge. The fully electrodynamic approach of Sec. IV is more readily generalizable than the method of Sec. III to the case of a tip of finite extent, and hence, has the potential to treat a more complete model of the measurement.

V. EXPERIMENTAL PROCEDURE

We next summarize the experimental procedures used to obtain the data discussed in Sec. VI. PMMA was obtained from Scientific Polymer Products (Cat. No. 942; Lot No. 01; atactic; molecular weight $M_w=145\,000$; polydispersity of $M_w/M_n \leq 1.05$) and was spin-cast from toluene into 280 nm thick films on epitaxial Au(111)-on-mica substrates (Agilent/Molecular Imaging; Part No. N9805B-FG). The resulting PMMA films were transferred to high vacuum (10^{-6} mbar) and annealed at 118 °C for 12 h to remove solvent and water.

Cantilevers were fabricated from $\langle 100 \rangle$ -oriented single-crystal silicon as described in Refs. 36 and 50. The cantilevers were approximately 250 μm long, 10 μm wide, and 340 nm thick; 100 μm from the end of each cantilever was a 20 $\mu\text{m} \times 20 \mu\text{m}$ hexagonal reflector pad, as shown in Fig. 1. As judged by scanning electron microscopy, the cantilever tip had a radius of approximately 30 nm. As in Ref. 17, the cantilever tip was coated with a 50 nm thick film of platinum over a 5 nm thick chromium adhesion layer using a shadow mask technique.³⁵ Cantilever displacement was detected with a custom-fabricated optical-fiber interferometer operating at 1310 nm. The interferometer used radio frequency current injection to reduce laser noise. The optical path length between the end of the fiber and the cantilever was controlled by varying the laser wavelength via adjusting the temperature of the laser with a thermoelectric cooler.⁵²

To detect the instantaneous cantilever frequency, the cantilever was driven into self-oscillation via positive feedback,¹³ as follows. The output of the interferometer's photodetector was passed through an *RLC* network (electrical quality factor ~ 10 ; electrical resonance frequency

~ 6 kHz) designed to phase shift the cantilever oscillation by 90°. The phase-shifted cantilever signal was then converted into a constant-amplitude square wave which drives a piezoelectric element underneath the cantilever. The resulting cantilever self-oscillation was digitized and transferred to a computer for subsequent analysis. The instantaneous cantilever frequency was determined from the digitized cantilever oscillation via a software frequency demodulator. Experiments took place at room temperature in high vacuum ($<10^{-6}$ mbar). Additional experimental details may be found in Ref. 53.

VI. FEASIBILITY OF JITTER MEASUREMENT ON A POLYMER FILM

We have derived expressions for three observables in electric force microscopy of a dielectric film: the noncontact friction coefficient in Eq. (3.13), the power spectrum of frequency jitter in Eq. (3.30), and the mean-squared frequency jitter in Eq. (3.32). The expression in Eq. (3.13) relates the noncontact friction coefficient to the absorptive and dispersive parts of the dielectric function at the cantilever frequency. This prediction for the variation of the noncontact friction coefficient with tip-sample separation, film thickness, and chemical identity, together with independently measured dielectric spectra, has already been shown to agree^{17,18} with measurements on polymer films. Here we establish that custom-fabricated high-sensitivity single crystal silicon cantilevers of the type used in Ref. 17 have more than sufficient sensitivity to detect the frequency fluctuations described here. According to Eq. (3.31), the power spectrum of the frequency jitter will be controlled by the low-frequency limit of the absorptive part of the dielectric function, as proposed by Israeloff *et al.*²⁷⁻³³ We postpone calculation of the full frequency dependence of the jitter power spectrum to a future comparison with measured results. Here we present two sets of experimental data. First, we show the low-frequency limit of the measured power spectrum of cantilever frequency fluctuations in the absence of a sample for a cantilever of the type used in Ref. 17. This quantity represents the minimum detectable frequency-fluctuation power spectrum at low frequencies in the presence of a sample. Second, we use this power spectrum measurement together with noncontact friction measurements over a PMMA film to estimate the minimum detectable mean-squared frequency jitter over this sample. The mean-squared jitter from PMMA predicted by Eq. (3.32) is shown to exceed this minimum for experimentally relevant tip-sample separations.

To facilitate discussion of measured quantities, we make two changes of notation from previous sections. First, angular frequencies ω will be replaced by frequencies $f=\omega/2\pi$. Second, we switch to *Système International* (SI) units so that, for example, the dimensionless dielectric constant of the previous sections is replaced by a dimensionless relative dielectric constant, defined as the ratio of the dielectric constant in SI units to the permittivity of the vacuum $\epsilon'_r(0) \equiv \epsilon'(0)/\epsilon_0$. The power spectrum of cantilever frequency fluctuations in Eq. (2.14) is then redefined as

$$P_{\delta f_c}(f) \equiv 4 \int_0^\infty dt \cos(2\pi ft) \langle \delta f_c(t) \delta f_c(0) \rangle. \quad (6.1)$$

Our prediction for this quantity may be obtained from Eq. (3.30) with the replacement of angular frequency by frequency, dielectric function by relative dielectric function, and squared cantilever tip charge by $q_c^2/4\pi\epsilon_0$. Applying this procedure to Eq. (3.32) yields our prediction for the mean-squared cantilever frequency fluctuation for sample thickness h and tip-sample separation d ,

$$\langle (\delta f_c)^2 \rangle = \int_0^\infty df P_{\delta f_c}(f), \quad (6.2)$$

$$= \left[\frac{3k_B T \zeta_r(0) q_c^2 f_c^2}{128 \pi \epsilon_0 k_c^2 d^5} \right] \int_0^\infty dq q^4 e^{-2q} \left[\frac{1 - e^{-4q(h/d)}}{1 + \zeta_r(0) e^{-2q(h/d)}} \right], \quad (6.3)$$

$$\zeta_r(0) \equiv \frac{\epsilon'_r(0) - 1}{\epsilon'_r(0) + 1}. \quad (6.4)$$

The power spectrum of frequency fluctuations is defined so that its integral over $f \in (0, \infty)$ yields the mean-squared fluctuation, as noted in Eq. (6.2).

Calculation of the static mean-squared frequency jitter from Eq. (6.3) requires only knowledge of the dielectric constant of the sample and of the tip-charge q_c . Since the measurement is carried out at constant voltage,^{17,18} q_c varies with d and must be determined from the capacitance C of the probe and sample by $q_c = CV_{ts}$. The friction calculations reported in Ref. 17 determined this capacitance by approximating the charged tip of the probe as a sphere of radius $R = 30$ nm located a distance d above a dielectric slab of thickness h backed by a conductor

$$C = 4\pi\epsilon_0 R \sum_{n=1}^\infty \frac{\sinh(\alpha)}{\sinh(n\alpha)}, \quad (6.5)$$

$$\alpha = \cosh^{-1} \left[1 + \frac{d}{R} + \frac{h}{\epsilon'_r(0)R} \right]. \quad (6.6)$$

In the limit $\epsilon'_r(0) \rightarrow 1$, this expression is exactly correct for a sphere of radius R with center a distance $R+d+h$ above a conducting plane.^{54,55} The replacement of h with $h/\epsilon'_r(0)$ is correct for a dielectric layer of thickness h within a parallel plate capacitor. The dielectric constant-dependent correction in Eq. (6.6) approximately accounts for the dielectric in the present configuration.

The smallest $P_{\delta f_c}(f)$ that can be detected experimentally is set by the magnitude of this quantity in the absence of the sample, which has been predicted to have the low-frequency limit^{13,46}

$$P_{\delta f_c}^{\min}(f) = P_{\delta f_c}^{\text{therm}} + p^{\text{det}} f^2, \quad (6.7)$$

$$P_{\delta f_c}^{\text{therm}} = \frac{k_B T}{2\pi^2 x_{\text{rms}}^2 k_c \tau}, \quad (6.8)$$

FIG. 2. Measured power spectrum of cantilever frequency fluctuations without a sample. Both axes are logarithmic. The solid line is a fit to Eq. (6.7). At the lowest frequencies, the power spectrum is a constant determined by thermomechanical fluctuations [dash-dot line; Eq. (6.8)]. At higher frequency, the spectral density of cantilever frequency fluctuations increases quadratically due to detector noise [dashed line; Eqs. (6.7)–(6.9)].

$$p^{\text{det}} = \frac{P_{\delta x}^{\text{det}}}{x_{\text{rms}}^2}. \quad (6.9)$$

This expression includes the effects of two uncorrelated sources of cantilever frequency noise. The first is thermomechanical white noise, which, in the limit of low frequency, gives the frequency-independent term in Eq. (6.8). This expression depends inversely on τ , the time for the cantilever to decay to $1/e$ of its initial amplitude after being excited. This ringdown time is related to the cantilever friction γ by $\gamma = k_c/(2\pi^2 f_c^2 \tau)$ and to the mechanical quality factor of the cantilever Q by $\tau = Q/(\pi f_c)$. The thermal contribution to the low-frequency power spectrum is inversely proportional to x_{rms}^2 , the mean-squared amplitude of the driven cantilever. The second contribution to $P_{\delta f_c}(f)$, quadratic in f , is detector noise, written in terms of an equivalent fluctuation of the cantilever coordinate x . Detector noise is also assumed to be white. The power spectrum of coordinate fluctuations $P_{\delta x}^{\text{det}}$ is independent of f at low frequencies, but the conversion from coordinate fluctuations to frequency fluctuations⁴⁶ introduces the f^2 dependence of Eq. (6.7). The contribution from detector noise is also inversely proportional to the mean-squared amplitude of the driven oscillator.

A representative frequency-fluctuation power spectrum for one of our high-sensitivity, custom fabricated, single crystal silicon cantilevers at room temperature in high vacuum can be seen in Fig. 2. The cantilever amplitude was $x_{\text{rms}} = 57$ nm. To obtain the spectrum of Fig. 2, 4 s of cantilever self-oscillation data were digitized and passed through a software frequency-demodulation algorithm. The power spectrum of each trace of cantilever frequency versus time was computed, after subtracting away the mean cantilever frequency of that trace. To obtain the plot of Fig. 2, 100 such power spectra were averaged. The resulting frequency-

fluctuation power spectrum was fit to Eq. (6.7) to obtain $P_{\delta f_c}^{\text{therm}} = 152.2 \pm 2.9 \times 10^{-6} \text{ Hz}^2/\text{Hz}$ and $p^{\text{det}} = 15.29 \pm 0.15 \times 10^{-9} \text{ Hz}^{-1}$. To check that the positive feedback electronics are not a significant source of cantilever frequency noise, an artificial self-oscillation signal was produced in software by adding a $x_{\text{rms}} = 57 \text{ nm}$ sine wave to digitized thermomechanical position fluctuations that had been observed with the positive feedback disengaged. A power spectrum nearly identical to that of Fig. 2 was obtained with $P_{\delta f_c}^{\text{therm}} = 205.2 \pm 2.7 \times 10^{-6} \text{ Hz}^2/\text{Hz}$ and $p^{\text{det}} = 19.68 \pm 0.15 \times 10^{-9} \text{ Hz}^{-1}$.

These values agree very well with those obtained by substituting independently measured cantilever and detector parameters into Eqs. (6.8) and (6.9). By fitting an average of 100 power spectra of cantilever position fluctuations, we obtain $f_c = 7073.286 \pm 0.077 \text{ Hz}$, $k_c = 4.02 \pm 0.15 \times 10^{-3} \text{ N/m}$, $Q = 1660 \pm 60$, and $P_{\delta x}^{\text{det}} = 64.32 \pm 0.23 \times 10^{-24} \text{ m}^2/\text{Hz}$. We infer a ringdown time of $\tau = Q/(\pi f_c) = 74.5 \pm 2.7 \text{ ms}$. By fitting the time decay of cantilever amplitude after disconnecting the cantilever from the positive feedback circuit, we obtain a second estimate, $\tau = 90.9 \pm 0.7 \text{ ms}$, for the ringdown time. From these parameters, $x_{\text{rms}} = 57 \text{ nm}$, and Eqs. (6.7) and (6.8), we estimate $P_{\delta f_c}^{\text{therm}} = 177\text{--}216 \times 10^{-6} \text{ Hz}^2/\text{Hz}$ and $p^{\text{det}} = 20.12 \pm 0.07 \times 10^{-9} \text{ Hz}^{-1}$, in excellent agreement with the values obtained by fitting the power spectrum in Fig. 2.

The agreement between the measured frequency power spectrum in Fig. 2 and the functional form in Eq. (6.7) establishes that for cantilever frequency deviations less than $f_{\text{therm}} \equiv (P_{\delta f_c}^{\text{therm}}/p^{\text{det}})^{1/2} \sim 100 \text{ Hz}$ away from f_c , detection sensitivity is limited only by thermomechanical position fluctuations of the cantilever and not by detector noise. Frequency deviations above f_{therm} can be observed, but sensitivity degrades sharply ($\propto f^2$) for $f > f_{\text{therm}}$. Increasing f_{therm} while maintaining cantilever sensitivity is possible, but would require replacing the fiber-optic interferometer used here with an even more sensitive displacement sensor.

We next apply the results of Fig. 2 to estimate the minimum detectable frequency jitter in order to demonstrate that the predicted root-mean-squared frequency jitter from a polymer thin film exceeds this threshold. The predicted root-mean-squared frequency jitter for a PMMA film of thickness $h = 280 \text{ nm}$ is shown as a function of tip-sample distance d by the dashed curve in Fig. 3. This result is calculated from Eq. (6.3) at $T = 298 \text{ K}$ with the dielectric constant¹⁷ for PMMA taken to be $\epsilon'_r(0) = 3.9$, cantilever force constant $k_c = 10^{-3} \text{ N/m}$, and resonant frequency $f_c = 5.920 \text{ kHz}$. The tip charge q_c is determined from the constant tip-sample voltage $V_{\text{ts}} = 0.5 \text{ V}$ and the capacitance in Eq. (6.5) with tip radius $R = 30 \text{ nm}$. The predicted jitter in Fig. 3 is seen to increase sharply with decreasing tip-sample distance. According to Eq. (6.3), for fixed tip charge, the jitter crosses over from d^{-6} for $d \gg h$ to d^{-5} for $d \ll h$. This dependence on d for constant q_c is modified by the d dependence of the tip charge at constant voltage, as shown in Eq. (6.5).

In a jitter measurement, the mean-squared variations in instantaneous frequency are observed for a time b^{-1} , with b the frequency bandwidth of the measurement. The mean-

FIG. 3. Predicted cantilever frequency jitter vs probe height. Note the logarithmic scale on both axes. The dashed line shows the calculated root-mean-squared frequency jitter from Eq. (6.3) for a cantilever having a tip radius of 30 nm held at 0.5 V over a 280 nm thick film of PMMA at room temperature. The solid line shows the minimum detectable frequency jitter calculated from Eq. (6.11) in a 100 Hz bandwidth, using known cantilever parameters and the measured height-dependent ringdown time.

squared frequency fluctuation determined from this measurement is given by the finite-bandwidth analog of Eq. (6.2),

$$\langle (\delta f_c)^2 \rangle = \int_0^b df P_{\delta f_c}(f). \quad (6.10)$$

The bandwidth b must be chosen large enough to capture most of the integral of the power spectrum. The data of Ref. 29 suggest that $b \leq 100 \text{ Hz}$ should suffice to include most of the frequency jitter generated by dielectric fluctuations in PMMA at room temperature. The analysis of Fig. 2 indicates that $b \leq f_{\text{therm}}$, so that the minimum detectable mean-squared jitter is given by^{13,46}

$$\langle (\delta f_c)^2 \rangle_{\text{min}} \approx b P_{\delta f_c}^{\text{therm}} = \frac{k_B T b}{2 \pi^2 x_{\text{rms}}^2 k_c \tau}. \quad (6.11)$$

Evaluation of the minimum detectable frequency jitter from Eq. (6.11) requires knowledge of the dependence of the cantilever ringdown time τ on tip-sample separation d . We have measured τ at room temperature over a 280 nm thick film of PMMA on an epitaxial Au(111) substrate. The measurements were carried out as detailed in Refs. 17 and 53. The cantilever was oriented with respect to the sample as sketched in Fig. 1 and had the same frequency and force constant given earlier for the calculation of the dashed curve in Fig. 3. This is a different cantilever from that employed in the experiments that produced Fig. 2. The solid curve in Fig. 3 shows the minimum detectable frequency jitter calculated from Eq. (6.11) with measured ringdown times. The root-mean-squared amplitude of the oscillations of the driven cantilever is $x_{\text{rms}} = 70 \text{ nm}$ and the frequency bandwidth is taken to be $b = 100 \text{ Hz}$.

Figure 3 demonstrates that the predicted frequency jitter from this polymer sample is at least an order of magnitude larger than the estimated minimum detectable jitter for easily achievable tip-sample separations $d \leq 200 \text{ nm}$. This finding implies that $P_{\delta f_c}(f)$ is likely to exceed $P_{\delta f_c}^{\text{therm}}$, especially at low frequencies at which the power spectrum should peak, over an even larger range of probe heights.

In this work we have presented a unified picture of two phenomena that can be probed in electric force microscopy: noncontact friction and frequency jitter. Both measurements are treated within a linear response framework, in which the charged probe reports on molecular motions in the sample that are unperturbed by the presence of the probe. The validity of this linear response picture for the noncontact friction was verified for the measurements in Ref. 17 by demonstrating that over the relevant range of tip-sample voltages V_{ts} in Fig. 1, the noncontact friction coefficient was quadratic in voltage, and hence, quadratic in tip-charge q_c , which is an identifying feature of a linear response treatment, as can be seen from Eq. (3.13). Within this linear response viewpoint, the friction coefficient is related to an equilibrium autocorrelation function of fluctuations of the electric field at the probe in Eq. (2.10) and the frequency jitter power spectrum is connected to an autocorrelation function of fluctuations in the field gradient in Eq. (2.14). Calculating these observables then requires a model from which the relevant correlation functions may be determined. We have treated the sample with utmost simplicity as a continuum slab governed by a linear dielectric function $\epsilon(\omega)$. We then demonstrated two complementary approaches for calculation of these correlation functions within the continuum model. The method of Sec. III employed a quasistatic approximation to electrodynamics, while the approach of Sec. IV employed full electrodynamics with a stochastic form of Maxwell's equations. Both methods agreed for the conditions appropriate to these measurements. The noncontact friction is determined by the dielectric response of the sample at the kHz frequency of the cantilever, while the frequency jitter power spectrum is driven by electric field fluctuations at low frequency.²⁷ We have already demonstrated that this approach reproduces well noncontact friction measurements for three polymers.^{17,18} It remains for future measurements of root-mean-squared frequency jitter and frequency jitter power spectra for several polymers to assess whether our predictions for these observables have the same validity.

Our results have two potential applications. First, they provide a means for predicting frequency jitter and friction that can limit the direct mechanical detection of very weak spin forces,^{34,56–58} and hence, may find application in designing such measurements. Second, they can be applied to interpret electric force microscopy as a local probe of dielectric fluctuations^{27–33} at surfaces. Since the present treatment models the sample as a dielectric continuum, the observables are related to bulk dielectric properties. An analysis that includes sample structure, for example, through a wave vector-dependent dielectric function,⁵⁹ will enhance the application of this technique to probe local molecular and charge carrier dynamics at surfaces.

ACKNOWLEDGMENTS

We acknowledge Seppe Kuehn for assistance in fabricating the cantilevers and in building the friction microscope used here. S.M.Y. acknowledges primary support from the National Science Foundation via the Cornell Center for Nanoscale Systems (EEC-0117770 and EEC-0646547) and

supplementary support from National Science Foundation Grant Nos. DMR-0134956 and DMR-0706508. This work was performed in part at the Cornell NanoScale Science and Technology Facility, a member of the National Nanotechnology Infrastructure Network, which is supported by the National Science Foundation through Grant No. ECS-0335765. J.A.M. acknowledges supplemental support from the National Institute of Health (5R01GM-070012), the Army Research Office Multi-University Research Initiative (W911NF-05-1-0403), and the National Science Foundation (DMR-0134956). R.F.L. acknowledges support from the National Science Foundation through Grant Nos. CHE0413992 and CHE0743299.

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